



Continued development and testing of a new thermodynamic aerosol module for urban and regional air quality models

Athanasios Nenes^a, Spyros N. Pandis^b, Christodoulos Pilinis^{c,*}

^a*Division of Marine and Atmospheric Chemistry, Rosenstiel School of Marine and Atmospheric Science, University of Miami, 4600 Rickenbacker Causeway, Miami, FL 33149, USA*

^b*Departments of Chemical Engineering and Engineering and Public Policy, Carnegie Mellon University, Pittsburgh, PA 15213, USA*

^c*Department of Environmental Science, University of the Aegean, Karadoni 17, Mytilene, GR-81100, Greece*

Received 26 August 1997; received in revised form 29 September 1998; accepted 1 October 1998

Abstract

A computationally efficient and rigorous thermodynamic model (ISORROPIA) that predicts the physical state and composition of inorganic atmospheric aerosol is presented. The advantages of this particular model render it suitable for incorporation into urban and regional air quality models. The model is embodied into the UAM-AERO air quality model, and the performance is compared with two other thermodynamic modules currently in use, SEQUILIB 1.5 and SEQUILIB 2.1. The new model yields predictions that agree with experimental measurements and the results of the other models, but at the same time proves to be much faster and computationally efficient. Using ISORROPIA accelerates the thermodynamic calculations by more than a factor of six, while the overall speed-up of UAM-AERO is at least twofold. This speedup is possible by the optimal solution of the thermodynamic equations, and the usage of precalculated tables, whenever possible. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Inorganic aerosols; Thermodynamic equilibrium module; Air quality models; Aerosol dynamics

1. Introduction

Knowing the physical state and composition of atmospheric aerosols is of great significance, especially when anthropogenic perturbations are examined, because of their role in atmospheric processes and climate forcing. Mathematical models which simulate the evolution of both gaseous and aerosol species have only recently started to appear, due to the complexity and variability of the processes in which particulate matter is involved.

Every aerosol model in some point is required to perform a thermodynamic equilibrium calculation. This is because mass transport of volatile species (e.g. water) between gas and aerosol phases is “driven” from the difference between ambient and equilibrium concentrations. Thus, a thermodynamic equilibrium module is an essential component of any aerosol model, and to a large extent determines the characteristics and efficiency of it. In essence, this implies that the thermodynamic module should be as accurate and fast as possible. Speed becomes a major issue for three-dimensional models, because of the computational burden associated with these type of calculations.

Literature offers a plethora of candidate thermodynamic equilibrium modules. Most of them, however, prove

*Corresponding author.

to be unsuitable, either because they cannot handle all the necessary species, or simply because they are too slow. It turns out that there is still need for codes that do not compromise speed for accuracy, are robust and able to efficiently handle the wide range of inputs encountered in a typical air quality run. Speed and numerical stability are valuable attributes, and particularly tough to achieve. Another weakness lies in the inadequate treatment of the transition from a dry to a wet aerosol. Soluble particles transform into an aqueous solution when the relative humidity reaches a specific level, characteristic of each salt. This relative humidity is called deliquescence relative humidity (DRH). A salt mixture behaves somewhat differently, and has a DRH which also depends upon the mixture composition and is always lower than the minimum DRH of each component. However, there is a minimum relative humidity, below which the aerosol is dry regardless of composition (Tang and Munkelwitz, 1993; Potukuchi and Wexler, 1995a, b). This relative humidity is known as mutual deliquescence relative humidity (MDRH), and is characteristic of the salt system (i.e., the type of salts in the mixture) and not composition. The system is said to be in a mutual deliquescence region (MDR), when the relative humidity is:

$$\text{MDRH}(\text{salt}_1, \text{salt}_2, \dots, \text{salt}_n) \leq$$

$$\text{RH} < \min\{\text{DRH}_{\text{salt}_1}, \text{DRH}_{\text{salt}_2}, \dots, \text{DRH}_{\text{salt}_n}\}.$$

Many times, for simplicity, MDRs are neglected, and the DRH is taken as the minimum DRH of the component salts. This simplification, however, alters the overall behavior of the system, since the presence of water drives volatiles in the aerosol phase and shifts the size distribution towards larger diameters. The aerosol behaves differently when the relative humidity is decreasing; it can be a supersaturated aqueous solution below the MDRH, and may crystallize only at a much lower humidity. This phenomenon is known as hysteresis effect, and depends on the dynamics of the system, so it cannot be addressed by thermodynamic codes.

This paper exhibits the usage of a new thermodynamic equilibrium aerosol module, ISORROPIA (Nenes et al., 1998) which resolves the problems previously addressed. Apart from considering mutual deliquescence regions, the solution process was optimized for speed and robustness. ISORROPIA is incorporated into an existing urban airshed model, UAM-AERO, which then is used to simulate atmospheric conditions in the South Coast Air Basin of California (SCAB) during the 24–25 June 1987 episode of the Southern California Air Quality Study (SCAQ). The simulations were repeated 3 times, using each time a different equilibrium module; versions 1.5 and 2.1 of SEQUILIB (Pilinis and Seinfeld, 1987) and ISORROPIA. The results obtained using the different equilibrium modules are then compared.

2. Description of ISORROPIA

ISORROPIA models the sodium–ammonium–chloride–sulfate–nitrate–water aerosol system. The aerosol particles are assumed to be internally mixed, meaning that all particles of the same size have the same composition. The possible species for each phase are:

Gas phase: $\text{NH}_3, \text{HNO}_3, \text{HCl}, \text{H}_2\text{O}.$

Liquid phase: $\text{NH}_4^+, \text{Na}^+, \text{H}^+, \text{Cl}^-, \text{NO}_3^-, \text{SO}_4^{2-}, \text{HSO}_4^-, \text{OH}^-, \text{H}_2\text{O}, \text{HNO}_{3(\text{aq})}, \text{HCl}_{(\text{aq})}, \text{NH}_{3(\text{aq})}, \text{H}_2\text{SO}_4.$

Solid phase: $(\text{NH}_4)_2\text{SO}_4, \text{NH}_4\text{HSO}_4, (\text{NH}_4)_3\text{H}(\text{SO}_4)_2, \text{NH}_4\text{NO}_3, \text{NH}_4\text{Cl}, \text{NaCl}, \text{NaNO}_3, \text{NaHSO}_4, \text{Na}_2\text{SO}_4.$

The number of viable species (thus, the number of equilibrium reactions solved) are determined by the relative abundance of each species and the ambient relative humidity. A more detailed description of the equilibrium reactions and the solution procedure of ISORROPIA is presented elsewhere (Nenes et al., 1998).

Special provision was taken in order to render ISORROPIA as fast and computationally efficient as possible. The number of iterations performed during the numerical solution largely determines the speed of the model. Hence, minimizing the number of equations needing numerical solution considerably reduces CPU time. With this in mind, the equilibrium equations for each case were ordered and manipulated so that analytical solutions could be obtained for as many equations possible. Adopting this approach, most cases could be solved using only one level of iteration. By comparison, SEQUILIB is more simplistic and potentially faster, but proves to be slower than ISORROPIA, mainly because SEQUILIB solves more equations numerically and uses nested iteration procedures of two (and sometimes three) levels when solving the equations. Another factor that speeds up ISORROPIA is the usage of precalculated tables, whenever possible.

ISORROPIA can currently handle two types of input:

- The total concentrations (i.e. gas and aerosol together) of sodium, ammonia, nitric acid, and sulfuric acid, together with the ambient relative humidity and temperature. This type of problem is termed “forward problem”.
- The concentrations of sodium, ammonium, nitrate, and sulfate in the aerosol phase, together with the ambient relative humidity and temperature. This type of problem is termed “reverse problem”.

The major improvements of ISORROPIA over the version presented by Nenes et al. (1998) is the incorporation of the undissociated species $\text{NH}_{3(\text{aq})}$, $\text{HNO}_{3(\text{aq})}$ and $\text{HCl}_{(\text{aq})}$ and the ability to solve “reverse problems”. The latter improvement is expected to be particularly useful,

since most of the available models cannot solve “reverse problems”.

3. Description of UAM-AERO – application to the SCAB

UAM-AERO is based on the air quality Urban Airshed Model Version IV (UAM-IV) (SAI, 1990a, b, c, d, e), with the following modifications:

(i) Gas-phase chemistry is replaced with a more flexible and easy to change mechanism (Kumar et al., 1995). (ii) Integration of gas-phase kinetics is done by using the high accuracy LSODE solver (Sun et al., 1994; Chock et al., 1994; Kumar et al., 1995). (iii) Sulfuric acid is produced from aqueous phase oxidation of sulfur dioxide. (iv) Condensable organics are produced using the yields reported by Pandis et al. (1992). (v) The gas-phase chemical kinetic rate expressions are calculated from three-dimensional temperature and water vapor concentration fields, and (vi) Dry-deposition is calculated using an algorithm based on Wesley (1989).

UAM-AERO currently incorporates three versions of SEQUILIB (Version 1.5, 2.0 and 2.1) for the thermodynamic calculations. Of the three modules, Version 1.5 is the fastest but least accurate, and 2.1 is the slowest but most accurate. The differences between versions lie mainly in the way activity coefficients are calculated. Version 2.1 calculates new activity coefficients in every iteration, while Version 1.5 stops calculating them whenever an approximate region containing the solution vector is found. This simplification significantly speeds up the calculations, but inevitably induces an error which can be large if the activity coefficients are sensitive to small changes in the ionic strength of the aqueous phase. Nevertheless, both versions are expected to have the same behavior, especially for high relative humidity environments.

The basecase run of Lurmann et al. (1997) for the 24–25 June 1987 episode of the SCAQS is repeated 3 times, once using SEQUILIB 1.5, once using SEQUILIB 2.1, and once with ISORROPIA. It should be noted that the “forward” mode of ISORROPIA is used in UAM-AERO.

4. Results

In order to evaluate the three aerosol modules, we compared predicted concentrations for all the sites used by Lurmann et al. (1997). We will present the results for the Central Los Angeles station against which traditionally air quality models have been tested. The runs simulate a time period of three days, between 23 and 25 June 1987. Even though results are shown only for the last day, the three day simulation period is necessary so that the effect of initial conditions on the aerosol composition

and size distribution are minimal. The runs were performed on a Hewlett-Packard 9000/715 workstation running HP-UX 9.05.

Fig. 1 presents the major meteorological parameters affecting the size composition distribution of atmospheric aerosols for 25 June 1987. The relative humidity and temperature curves are antisymmetric, which indicates a lack of significant mixing of air masses near the site, for that day. The plot also shows the deliquescence relative humidity of ammonium nitrate, below of which defines a dry aerosol for SEQUILIB, and an MDRH region for ISORROPIA.

Fig. 2 is the plot of aerosol nitrate for 25 June 1987. SEQUILIB 1.5 and SEQUILIB 2.1 predict the same amount of PM_{10} nitrate, while ISORROPIA, especially during midday, calculates lower concentrations. This difference is attributed to the equilibrium constants used for in the nitrate equilibria. During early morning (midnight–8 a.m.) and night (8 p.m.–midnight), the aerosol contains enough water to dissolve most of the nitrate gas phase, so differences are not significant. The discrepancies however maximize around midday, where relative humidity drops below the deliquescence point of ammonium nitrate, and the aerosol dries up considerably. To prove that the differences are largely due to the equilibrium constants, another simulation was performed using ISORROPIA but with the nitrate equilibrium constants of SEQUILIB. The results of this run are shown in Fig. 2 and it can be seen that ISORROPIA and SEQUILIB yield very similar results. Any minor differences are attributed to the different activity coefficient models used.

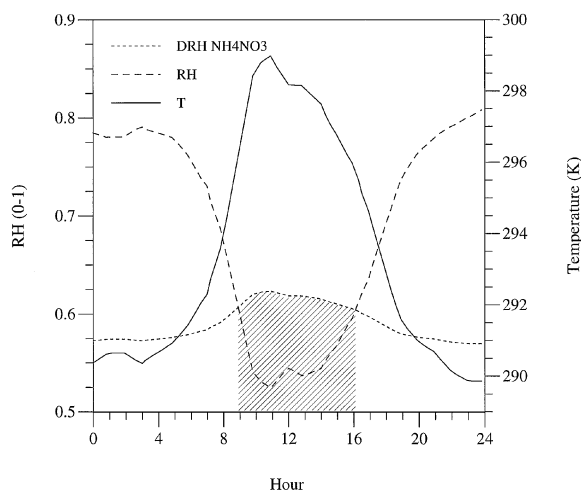


Fig. 1. Ambient temperature, relative humidity and ammonium nitrate DRH profiles at Central Los Angeles, for 25 June 1987. The shaded area denotes a MDR, for which SEQUILIB assumes a dry aerosol, while ISORROPIA still presumes it being wet.

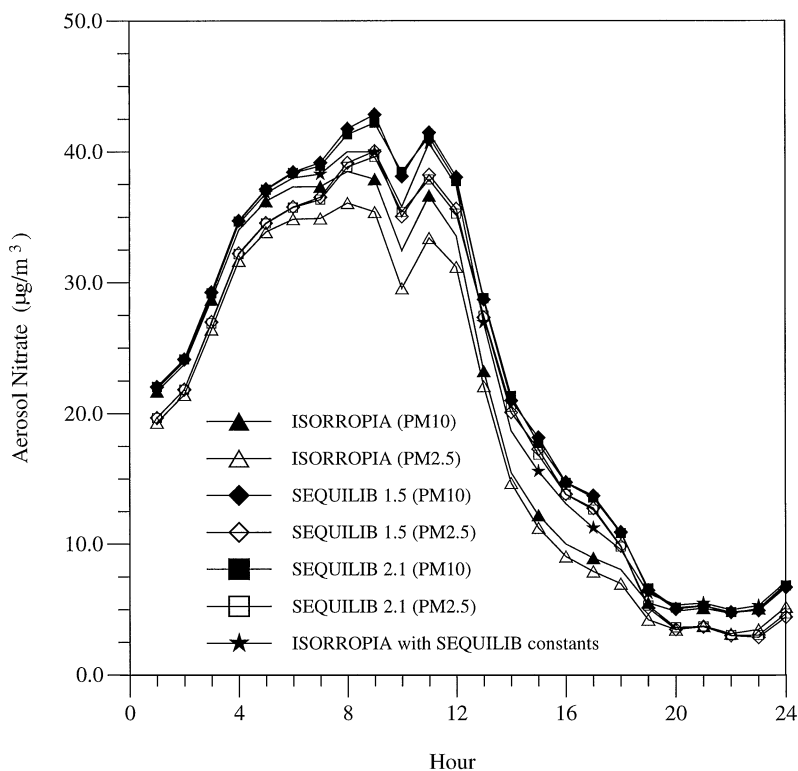


Fig. 2. Predicted nitrate concentrations at Central Los Angeles for 25 June 1987.

Fig. 3 is the plot of aerosol sulfate for 25 June 1987. As one can observe, all three models predict the same amount of PM_{10} sulfate. This is expected because sulfates are not volatile and reside completely in the aerosol phase, so the amount of it depends mainly on chemistry and not thermodynamic partitioning. Similar things could be said for $PM_{2.5}$ sulfate. Small differences are seen around 12 p.m., where SEQUILIB seems to predict more sulfate mass than ISORROPIA. SEQUILIB, because it predicts more aerosol nitrate, tends to calculate more aerosol water during the morning hours. This means that the aerosol has larger droplets, so more H_2SO_4 condenses on large particles. Thus, when relative humidity drops, the aerosol loses water and the size distribution shifts towards smaller diameters and, more sulfate shows up in the $PM_{2.5}$ fraction. This excess in $PM_{2.5}$ sulfate vanishes later, when the particles regain water (because relative humidity increases), shifting the sulfates towards larger diameters.

The total CPU time needed by UAM-AERO, as much as the time required by the equilibrium calculations are given in Table 1. It immediately becomes apparent that ISORROPIA significantly speeds up UAM-AERO. Less than 20% of the total CPU time is devoted to equilibrium calculations, which is much less than what SEQUILIB 1.5 (58%) and SEQUILIB 2.1 (93%) demand.

Another characteristic of ISORROPIA is that computation time is not affected by large variations in relative humidity and concentrations. This is very important, because any type of conditions can be simulated with the same computational efficiency. On the other hand, both versions of SEQUILIB do not show this type of behavior, but slow down in the presence of an aqueous phase. Fig. 4a–c plot the cumulative CPU time required by the three equilibrium models during the simulated day. The slope denotes the amount of time needed by the thermodynamic module for each hour simulated by UAM-AERO. Until 8 a.m., ISORROPIA needs 235.5 CPU seconds per simulation hour (Fig. 4a). This amount of time slightly increases to about 287 CPU seconds after 8 a.m. However, the two rates are very close to each other, and one can say that the time needed by ISORROPIA for the equilibrium calculations is essentially the same. The corresponding plots for SEQUILIB 1.5 and SEQUILIB 2.1 are shown in Fig. 4b and c, respectively. Three regimes are discerned in these plots, one between midnight and 9 a.m., one between 9 a.m. and 8 p.m., and one from 8 p.m. to midnight. Each of these regimes differ in the CPU time needed per simulation hour, being very large during morning and evening hours and less during midday. During the first and third regime, relative humidity is high and the aerosol is composed of an aqueous

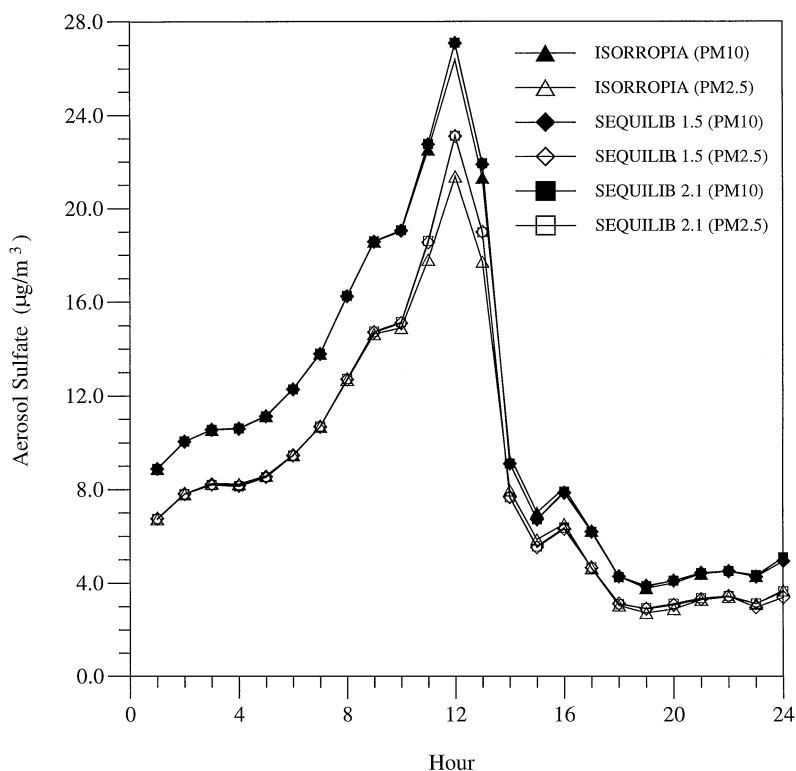


Fig. 3. Predicted sulfate concentrations at Central Los Angeles for 25 June 1987.

Table 1
Absolute and relative execution times for the 23–25 June run

Equilibrium model	Total CPU time for run (s)	CPU time for equilibrium calculations (s)	% of total CPU time used for equilibrium calculations	$\frac{t_{\text{MODEL}}}{t_{\text{ISORROPIA}}}$
ISORROPIA	37 477	6664	17.8	1.0
SEQUILIB 1.5	71 267	41 512	58.2	6.2
SEQUILIB 2.1	281 301	261 649	93.0	39.3

phase. This implies that activity coefficients have to be calculated, which increase the computational burden. During midday (second regime), the relative humidity drops significantly, the aerosol dries up, and activity coefficients are not calculated so the solution process is accelerated. It should be noted that for each version of SEQUILIB, the first and third regimes have essentially the same slopes, which further supports that the difference in CPU time is from the activity coefficient calculations. Finally, one must point out that ISORROPIA needs much less time for calculations than both versions of SEQUILIB, particularly when the relative humidity is high.

Predicted and measured mean 24 h average concentrations for the eight SCAQS stations are shown in Table 2. The observed values were obtained from Lurmann et al. (1997). In general, all three thermodynamic modules yield similar results. ISORROPIA yields better predictions for aerosol ammonium and $\text{PM}_{2.5}$ nitrate, while SEQUILIB seems to perform better in PM_{10} nitrate. The error in sulfate is essentially the same, while the chlorides are always underpredicted. For PM_{10} chloride, SEQUILIB 2.1 seems to yield worse results than SEQUILIB 1.5. This is expected because most of the SCAQS stations reside near coastal regions where SEQUILIB 2.1 predicts higher values of aerosol chloride than SEQUILIB 1.5. Apart

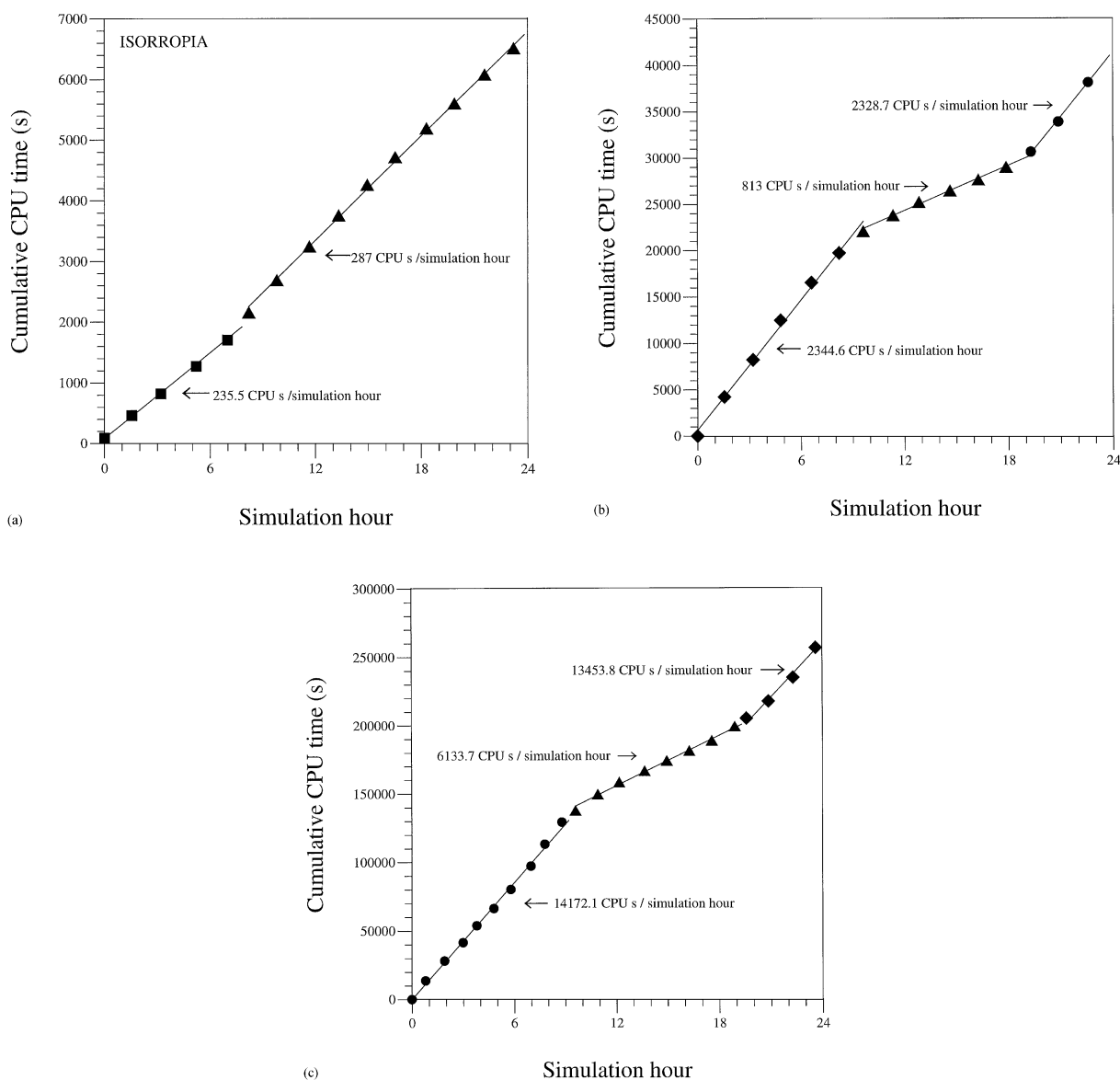


Fig. 4. Cumulative CPU time needed by (a) ISORROPIA, (b) SEQUILIB 1.5, (c) SEQUILIB 2.1, for 25 June 1987.

from the absolute error of each prediction, all three models display the same type of error, that is, all of them overpredict or underpredict. This systematic behavior is probably the result of factors other than those associated with the thermodynamic modules, i.e. the simplified aerosol dynamics solved by UAM-AERO.

5. Summary and conclusions

This paper presents a comprehensive and computationally efficient equilibrium aerosol model, called ISOR-

ROPIA, which is very suitable for urban and regional air quality models. ISORROPIA was incorporated into the UAM-AERO airshed model, and the basecase run of Lurmann et al. (1997) was performed. The results then were compared with experimental measurements and with the predictions of UAM-AERO using two other thermodynamic modules currently in use, SEQUILIB Version 1.5 and SEQUILIB Version 2.1. The three models generally agree in their predictions, and are in good agreement with experimental results. Any disagreement between the models was credited to differences in the equilibrium constants used (mainly in the equilibrium

Table 2

UAM-AERO model performance on the mean 24 h average concentrations ($\mu\text{g m}^{-3}$) of the eight SCAQS stations (25 June 1987). The parentheses contain the % errors

Species	Mean observed value	ISORROPIA prediction	SEUILIB 1.5 prediction	SEUILIB 2.1 prediction
PM _{2.5} NO ₃	15.8	16.3 (3.2)	18.4 (16.5)	18.3 (15.8)
PM ₁₀ NO ₃	21.7	18.5 (− 14.7)	20.6 (− 5.1)	20.5 (− 5.5)
PM _{2.5} NH ₄	5.9	8.1 (37.3)	8.8 (49.2)	8.8 (49.2)
PM ₁₀ NH ₄	8.9	8.9 (0.0)	9.5 (6.7)	9.4 (5.6)
PM _{2.5} SO ₄	10.6	8.8 (− 17.0)	9.0 (− 15.1)	9.0 (− 15.1)
PM ₁₀ SO ₄	12.3	11.1 (− 9.8)	11.1 (− 9.8)	11.1 (− 9.8)
PM ₁₀ Na	1.5	1.5 (0.0)	1.5 (0.0)	1.5 (0.0)
PM ₁₀ Cl	1.0	1.4 (40.0)	1.2 (20.0)	1.5 (50.0)

between solid ammonium nitrate and its gas precursors), and the calculated activity coefficients, whenever an aqueous phase was present. The Mutual Deliquescence Regions of ISORROPIA also contribute to differences, since in this case, the predicted equilibrium state of the aerosol is fundamentally different between models.

The uncertainties associated with the model inputs and measurements inhibit one to conclusively decide on the superiority of any particular model, at least from a statistical point of view. Nevertheless, one can definitely say that the usage of ISORROPIA yields similar predictions to those of SEUILIB. Combining this with the fact that ISORROPIA, while lacking most of the simplifying assumptions used in SEUILIB, is also significantly faster and computationally efficient, makes ISORROPIA a very reliable and efficient thermodynamic module, and is recommended for usage in urban and regional air quality models.

Acknowledgements

This research was conducted with support from the Environmental Protection Agency under grant R-824793010 and from the National Science Foundation under grant ATM-9625718.

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